

The University of Chicago

THE EFFECT
OF METALS ON THE ADDITION
OF HYDROGEN BROMIDE TO
OLEFINIC SUBSTANCES

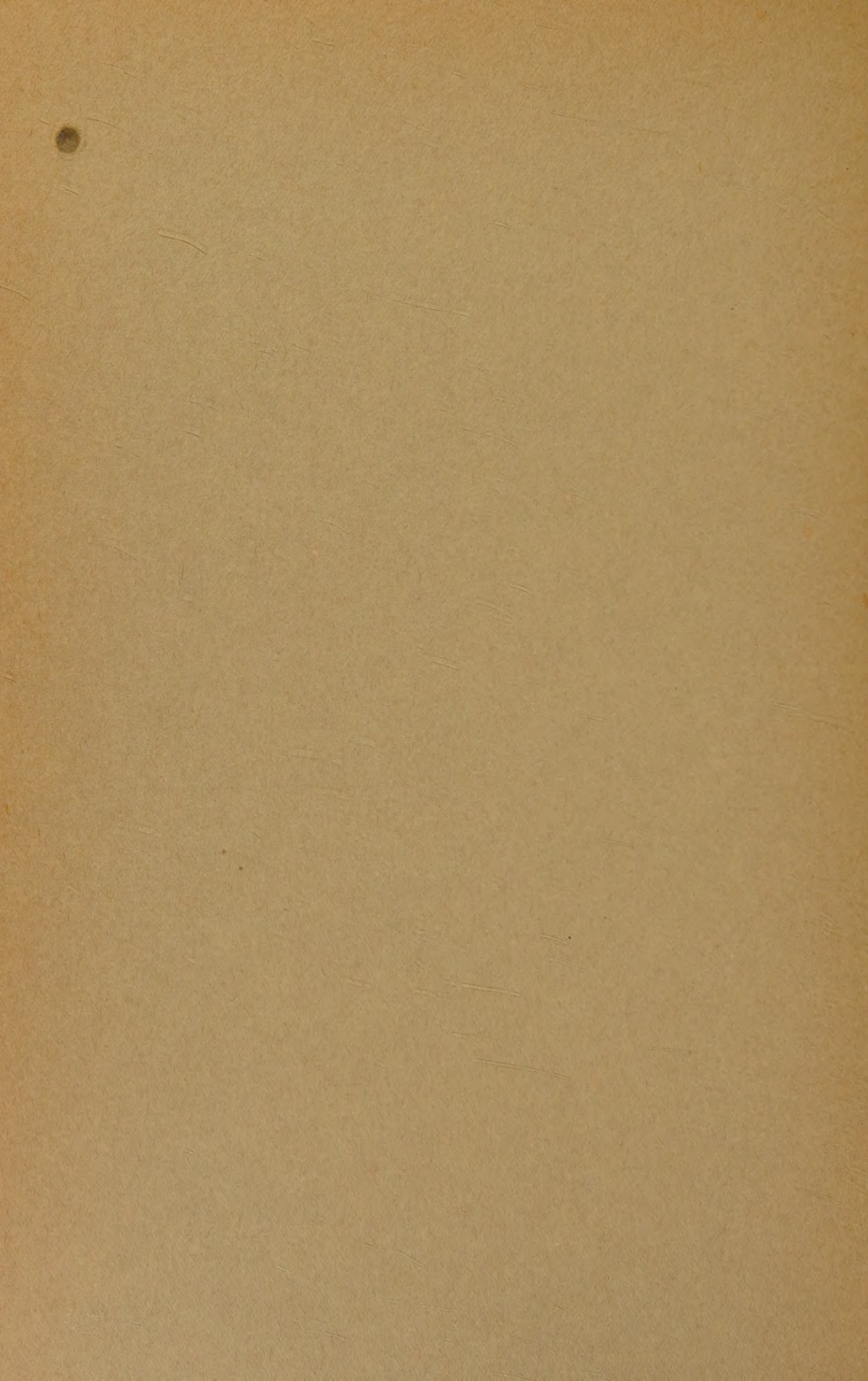
A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
DECEMBER, 1939

By
WALTER R. HAEFELE

CHICAGO, ILLINOIS

1945



The University of Chicago

THE EFFECT
OF METALS ON THE ADDITION
OF HYDROGEN BROMIDE TO
OLEFINIC SUBSTANCES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
DECEMBER, 1939

By
WALTER R. HAEFELE

CHICAGO, ILLINOIS

1945



THE EFFECT OF METALS ON THE ADDITION OF HYDROGEN
BROMIDE TO OLEFINIC SUBSTANCES

INTRODUCTION

In 1933 Kharasch and Mayo¹ reported that the addition of hydrogen bromide to allyl bromide could take place in two ways depending on the conditions under which the reaction was carried out. The normal addition, which produced 1,2-dibromopropane, occurred in the absence of oxygen or light. When oxygen or peroxides were present, abnormal addition ensued, with the formation of 1,3-dibromopropane.

In 1936 Urushibara and Takebayashi² reported that finely divided metallic iron, nickel, or cobalt included in the reaction mixtures with allyl bromide and hydrogen bromide would cause abnormal addition. They claimed that these metals remained unchanged during the addition reaction, and concluded that the effect of metals must be entirely physical. Since these metals and oxygen all had high paramagnetic susceptibilities, they suggested that abnormal addition occurred only when paramagnetic substances were present. They stated that, "although what change occurs in the molecule of allyl bromide under the influence of metals and oxygen is unknown, it can be said that the ordinary form preferring the normal addition is changed into an extraordinary form preferring the abnormal addition."³ They suggested that 3,000 or more molecules of allyl bromide were included in the "sphere of influence" about an oxygen or metal atom.⁴ Hydrogen bromide added rapidly to these influenced molecules to form 95 per cent 1,3-

¹M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

²Urushibara and Takebayashi, Bull. Chem. Soc. Japan, 11, 692 (1936).

³Urushibara and Takebayashi, ibid., 12, 173 (1937).

⁴Ibid.

dibromopropane and 5 per cent 1,2-dibromopropane. The atoms of the metal were supposed to have a much larger sphere of influence than oxygen atoms. It was also maintained by these authors that the "strength or freshness of the oxygen influence affects only the rate of addition and not the proportion of products obtained."

However, the idea of paramagnetic influence as a cause for abnormal addition is not consistent with all the available data. Urushibara and Takebayashi⁵ reported that neither man-ganous sulphate nor platinum black would cause abnormal addition, although these substances are paramagnetic. The inhibiting effect of certain substances on the abnormal addition is not explicable on the basis of this theory. It was demonstrated by Kharasch and Mayo that small amounts of diphenylamine, thiocresol, hydroquinone, or mercaptobenzothiazol⁶ would inhibit the abnormal addition caused by oxygen or peroxides, and Urushibara and Takebayashi report that catechol and hydroquinone inhibit the abnormal addition caused by nickel.⁷

The possibility that the paramagnetic properties of oxygen are responsible for the unusual results obtained with that molecule was considered by Kharasch and Mayo, but rejected when only normal addition was obtained in the presence of highly paramagnetic substances such as nitric oxide and nitrogen dioxide.⁸ The results of the present study indicated definitely that metals do not remain unattacked in reaction mixtures of allyl bromide and hydrogen bromide, contrary to the statements of Urushibara and Takebayashi. Hence the purely physical explanation for the effect of metals in causing abnormal addition seems improbable. The interpretation of the effect of metals as a chain reaction initiated by hydrogen atoms and carried on by bromine atoms seems to explain best the data recorded in the literature, as well as the new data set forth in this paper. The bromine atom mechanism was suggested previously by Kharasch, Engelmann, and Mayo.⁹

⁵Urushibara and Takebayashi, ibid., 11, 692 (1936).

⁶Kharasch and Mayo, loc. cit.

⁷Urushibara and Takebayashi, Bull. Chem. Soc. Japan, 13, 404 (1938).

⁸Kharasch and Mayo, loc. cit.

⁹Kharasch, Engelmann, and Mayo, J. Org. Chem., 2, 288 (1937).

After the present work was finished Urushibara and Simamura¹⁰ published a short review of the peroxide effect in which they repudiated their physical explanation for the effect of metals and oxygen in initiating abnormal addition, and adopted the bromine atom mechanism mentioned above for the action of oxygen. However, they represented the normal addition of hydrogen bromide as a chain reaction carried along by hydrogen atoms. They stated that in a future paper they would apply these ideas to the action of metals on addition.

In any addition, it was their belief that two chain reactions occurred simultaneously--the one leading to normal and the other to abnormal addition. A preponderance of one type of addition was only found when an inhibition of the other type had occurred. It seems improbable that the normal addition can be demonstrated to be a chain reaction; in fact, the only evidence which Urushibara and Simamura present is the "inhibition" of the normal addition under peroxidic conditions. This apparent inhibition is just as easily explained in terms of relative reaction rates, since the abnormal addition is known to be several hundred times faster than the normal addition. Inasmuch as this difference in speeds exists, it is not surprising that little normal addition should be observed when most of the reactants are being used up by the abnormal addition. It is also doubtful whether the idea that the normal reaction is a chain reaction can be supported thermodynamically, since the hydrogen atoms which Urushibara supposes to carry along the normal addition must become attached to the double bond in an ethylenic molecule and form an ion. The ion formed here has not enough energy to cleave a molecule of hydrogen bromide, which is a necessary reaction to complete the normal addition and form another hydrogen ion to continue the chain.

The hypothesis advanced as a result of the present study, that is, that metals cause abnormal addition by generating hydrogen atoms, was tested by several series of experiments. It was first shown that iron was attacked in anhydrous mixtures of allyl bromide and hydrogen bromide to form ferrous bromide and hydrogen, but that mostly abnormal addition took place in these experiments.

¹⁰Urushibara and Simamura, Bull. Chem. Soc. Japan, 14, 323 (1939).

A second test of this hypothesis was an attempt to obtain results with other metals similar to those found with iron, in order to demonstrate that both paramagnetic and diamagnetic metals would initiate abnormal addition. This could not be shown, since it was found that not only the metal but its metal halide were important factors in influencing addition, and that paramagnetism could hardly be a factor in cases where all or most of the metal reacted to form its corresponding metal bromide. The final portion of the present work was an investigation of the catalytic effects of metal halides on the normal addition, of the effects of organic antioxidants and of metal halides in inhibiting abnormal addition initiated either by oxygen or a metal, and of the influence of iron on the addition of hydrogen bromide to other organic molecules. From this evidence a comprehensive picture of the effects of metals was built up, and used to correlate all the data which has so far appeared in the literature.

DISCUSSION OF RESULTS

INDICES OF REFRACTION OF THE DIBROMOPROPANES

An extensive study was made of the refractive indices of the dibromopropanes on materials purified with the aid of an efficient Podbielniak fractionating column. As shown in the experimental part, constant boiling fractions of pure 1,2- and 1,3-dibromopropanes had indices of refraction (n_D^{20}) 1.5200 and 1.5231 respectively, as compared with 1.5194 and 1.5232 given by Kharasch and Mayo.¹¹ The percentage of 1,3-dibromopropane given by them (per cent KM) in the range 16-97 per cent may be converted to the corrected value (per cent KHM) through the formula

$$3.22 \left(\frac{\text{per cent KM}-6}{2.63} \right) = \text{per cent KHM}$$

Table 1 indicates present success in checking the work of Kharasch and Mayo. The addition of hydrogen bromide to peroxide-free allyl bromide in the absence of air, with or without diphenylamine as antioxidant, yielded a dibromide with the same index as they reported. However, although they estimated the addi-

¹¹Kharasch and Mayo, loc. cit.

tion products to contain about 10 per cent 1,3-dibromopropane, the new refractive indices show that the product was pure 1,2-dibromopropane.

In the presence of benzoyl peroxide, ascaridole, or air abnormal addition predominated with hydrogen bromide and allyl bromide. These experiments provide the basis for comparison of the oxygen and peroxide effect with the effect of metals.

TABLE 1

THE PEROXIDE EFFECT IN THE ADDITION OF
HYDROGEN BROMIDE TO ALLYL BROMIDE

Expt. No.	Conditions of Addition ^a			Product		Remarks
	Mols HBr ^b	Time (Days)	Air	Yield (Per Cent)	1,3-di- bromo- propane ^c (Per Cent)	
29	1.5	8	-	67	0	
38	1.5	8	-	71	0	
2	1.7	13	-	98	0	0.3 mol per cent Ph ₂ NH
7	1.5	2	+	94	80	
21	1.5	3	+	98	80	0.3 mol per cent Bz ₂ O ₂
22	1.3	5	-	84	87	0.3 mol per cent Bz ₂ O ₂
1	1.5	7	+	94	61	0.15 mol per cent ascaridole
104	1.3	1	+	98	91	Shaken
107	1.3	1	+	97	94	Shaken

^aReaction took place at room temperature in the absence of solvents or light.

^bPer mol allyl bromide.

^cRemainder of addition product was pure 1,2-dibromopropane.

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL
BROMIDE IN THE PRESENCE OF IRON

Experiments with freshly reduced iron, allyl bromide, and hydrogen bromide in the absence of air, peroxides, and light confirmed the conclusions of Urushibara and Takebayashi that considerable abnormal addition took place.^{12, 13} Table 2 shows that when the reaction mixtures were agitated (shaking machine) addition was practically complete in 1-2 hours, and that the product was 85-100 per cent 1,3-dibromopropane. The iron (1.5 grams per 10 grams allyl bromide) did not change its appearance during most of these additions, but bromide analyses on inorganic residues indicated that the iron always reacted with the hydrogen bromide, sometimes to the extent of 25 per cent.

However, when the reaction mixtures containing iron were not agitated, quite different results were obtained, as shown in Table 3. The addition reaction took place about 1/25 as rapidly as in the agitated experiments, completion being attained in one to three days. The addition products were mixtures of both dibromopropanes in which the proportion of the 1,3-compound varied from 30 to 80 per cent. In each experiment the iron became covered with a green layer of ferrous bromide to the extent of 80 per cent of the initial iron. Hydrogen pressures as high as ten atmospheres were noted when such reaction tubes were opened.

In the above series of experiments, abnormal addition was invariably accompanied by the formation of hydrogen and ferrous bromide. Other experiments to be described will show that ferrous bromide cannot be responsible for abnormal addition, and therefore that the iron itself or the production of hydrogen from it must initiate the abnormal reaction.

The experiments with iron suggest a mechanism by which metals affect the addition of hydrogen bromide to unsaturated substances. Since iron reacts with hydrogen bromide, its effect need not be purely physical, as Urushibara and Takebayashi suggested.

¹²Urushibara and Takebayashi, Bull. Chem. Soc. Japan, 11, 692 (1936).

¹³Urushibara and Takebayashi, ibid., 12, 51 (1937).

TABLE 2

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL
BROMIDE IN THE PRESENCE OF IRON

Expt. No.	Conditions of Addition ^a				Products	
	Mols HBr ^b	Mols Fe ^b	Fe Reacted (Per Cent)	Reaction Time ^c (Hours)	Yield (Per Cent)	1,3-di- bromopropane ^d (Per Cent)
63	1.2	0.31	11	72	100	87
73	1.3	0.02	18	16	90	94
68	1.4	0.30	10	72	100	94
71	1.0	0.32	8	72	91	94
69	1.3	0.30	13	72 ^e	100	97
74	1.3	0.32	6	18 ^f	100	97
75	1.3	0.32	4	4 ^g	64	97
70	3.3	0.41	23	24	100	97
116	1.3	0.32	11	1	59	97

^aExperiments in vacuo and shaken mechanically.

^bPer mol allyl bromide.

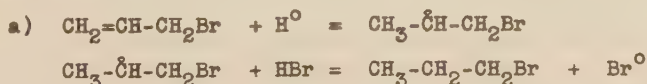
^cAt room temperature in the absence of light, air, and solvents.

^dRemainder of addition product was 1,2-dibromopropane.

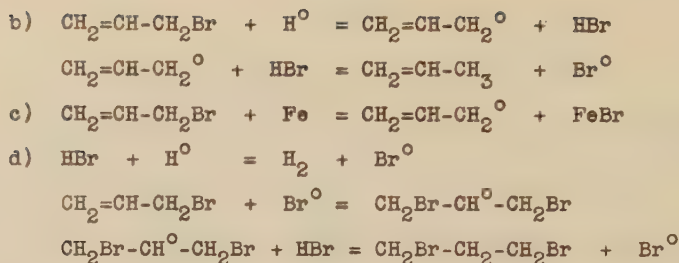
^eComplete in two hours. ^fComplete in one hour.

^gTemperature was -2°C.

The occurrence of hydrogen among the reaction products led to the conclusion that hydrogen atoms are probably the actual initiators of abnormal addition. These hydrogen atoms could generate bromine atoms by any one of the following mechanisms, and subsequent addition could occur by the bromine atom mechanism suggested by Kharasch, Engelmann, and Mayo:¹⁴



¹⁴Kharasch, Engelmann, and Mayo, loc. cit.



We have no reason for preferring any one of these mechanisms, since possibly all contribute to abnormal addition.

TABLE 3
THE ADDITION OF HYDROGEN BROMIDE TO ALLYL
BROMIDE IN THE PRESENCE OF IRON

Expt. No.	Conditions of Addition				Products	
	Mols HBr ^a	Mols Fe ^a	Fe Reacted ^b (Per Cent)	Reaction Time ^c (Days)	Yield (Per Cent)	1,3-di- bromopropane ^d (Per Cent)
31	1.5	0.32	23	4	97	26
18	1.6	0.32	33 (31)	6	97	30
23	1.5 ^e	0.32	22 (22)	3	100	30
32	1.5	0.32	15	3	98	39
30	1.6	0.32	31	3	93	48
27	1.6	0.32	16	3	98	58
28	1.6	0.32	11	3	98	58
14	1.5	0.32	82	4	99	61
12	1.6	0.32	20 (16)	6	94	61
11	1.5	0.32	42 (35)	7	94	77

^aPer mol of allyl bromide.

^bDetermined volumetrically from bromide ion. Numbers in parentheses are values from hydrogen produced.

^cAt room temperature in the absence of solvents, air, and light.

^dRemainder of addition product was 1,2-dibromopropane.

^e0.1 g. phosphorus pentoxide added.

The effectiveness of agitation in promoting abnormal addition in the presence of iron may be explained by the distribution and coating of iron particles. Agitation should result in a greater amount of reaction of the iron by removing the ferrous bromide coating formed on its surface, thus initiating more bromine atom chains. Further, by having the iron suspended through the solution, a chain, once started, should be propagated further because the possible chain breakers, e.g., iron, H atoms, Br atoms, and organic radicals, are less likely to be within interfering distance.

EFFECT OF INHIBITORS

Kharasch and Mayo first showed that the abnormal addition of hydrogen bromide to allyl bromide could be inhibited by certain organic substances such as diphenylamine and hydroquinone.¹⁵ Urushibara and Takebayashi¹⁶ found that abnormal addition caused by nickel was completely inhibited by catechol and hydroquinone, but only partially by diphenylamine. Table 4 confirms their findings and shows further that the iron-initiated addition did not occur in the presence of catechol or thiocresol, but that only partial inhibition could be demonstrated with phenol, resorcinol, or diphenylamine. Nevertheless, in all of these experiments the reaction between iron and hydrogen bromide proceeded to the same extent as in experiments in which no inhibitor was present. Accordingly, it is clear that inhibition did not occur through the suppression of the reaction between iron and hydrogen bromide.

The effect of organic inhibitors is explicable on the basis that they react with bromine atoms with varying ease, and thus break the chains in abnormal addition with different degrees of efficiency. Solubility was also a factor in the case of diphenylamine, which could be observed in the reaction mixture as the crystalline hydrobromide. The relative efficiency of the o- and m- dihydroxybenzenes seemed to follow their well-established antioxidant properties.

In the course of this study it was discovered that some

¹⁵Kharasch and Mayo, loc. cit.

¹⁶Urushibara and Takebayashi, Bull. Chem. Soc. Japan, 13, 404 (1938).

metal halides will inhibit abnormal addition quite as well as organic substances. Their relative effectiveness was tested by placing the metal bromides in reaction mixtures containing air or iron. These mixtures, unless inhibition occurred, would yield abnormal addition almost exclusively.

TABLE 4

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE
IN THE PRESENCE OF IRON AND ANTIOXIDANTS

Expt. No.	Conditions of Addition					Products	
	Mols HBr ^a	Mols Fe ^a	Fe Reacted (Per Cent)	Antioxi- dant (Mol Per Cent)	Time (Days) ^b	Yield (Per Cent)	1,3-di- bromo- propane ^c (Per Cent)
5	1.5	0.32	..	3 Ph ₂ NH ^d	5	88	32
10	1.5	0.30	38	3 Ph ₂ NH	11	98	43
81	1.3	0.32	25	3 Ph ₂ NH	1 ^e	71	61
17	1.5	0.32	17	3 catechol	4	98	0
82	1.3	0.32	9	3 catechol	1 ^e	63	0
42	1.5	0.32	52	4 phenol	3	78	17
65	1.5	0.31	20	3 resorcinol	5	78	13
84	1.3	0.31	49	3 thiocresol	0.75 ^e	63	0

^aPer mol allyl bromide.

^bReaction took place at room temperature in the absence of solvents, air, and light.

^cRemainder of addition products was 1,2-dibromopropane.

^dCareful purification in vacuo failed to increase the efficiency of the diphenylamine.

^eShaken mechanically.

Table 5 shows the gradations in efficiency of inhibition which were noted. Ferrous, nickelous, and cobaltous bromides prevented abnormal addition in the presence of air but not in the presence of iron. Stannous and cuprous bromides inhibited abnormal addition started either by iron or air. Stannous bromide (formed from tin in the reaction mixture, or added at the beginning) acted as an inhibitor on abnormal addition started by air (111), by iron (110), or by tin itself (88, 106), but did not inhibit such addition when air and tin were present together (100, 108, 119). It was demonstrated indirectly that cadmium and lead bromides were inhibitors by placing the corresponding metal in a reaction mixture with air. In this case the metal reacted with hydrogen bromide to form the metal bromide, which inhibited the air-initiated abnormal addition.

Some metal bromides showed an accelerating action on the normal addition: stannous, zinc, ferrous, cobaltous. Other metal bromides, such as cuprous and nickelous bromides, showed little, if any, acceleration. The extent of acceleration can be noted in Table 5 by comparing the yield in any experiment with a blank, No. 38.

That metal bromides are inhibitors for abnormal addition, and in some cases accelerators for normal addition, is important in explaining why some metals do and others do not cause abnormal addition, as elaborated in the next section.

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF OTHER METALS

Urushibara and Takebayashi¹⁷ showed that iron, nickel, and cobalt promoted abnormal addition of hydrogen bromide to allyl bromide, but that platinum black had no effect.¹⁸ In order to test the effect of other than Group VIII metals on addition reactions zinc, lead, titanium, arsenic, copper, silicon, cadmium,

¹⁷Urushibara and Takebayashi, Bull. Soc. Chem. Japan, 12, 51 (1937).

¹⁸Urushibara and Takebayashi, ibid., 11, 692 (1936).

TABLE 5

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE
IN THE PRESENCE OF METALS AND METAL BROMIDES

Expt. No.	Conditions of Addition					Products	
	Mols Added ^a Substance	Metal Reacted (Per Cent)	Mols HBr ^a	Time (Days) ^b	Air	Yield (Per Cent)	1,3-di- bromo- propane ^c (Per Cent)
38	..	..	1.5	8 ^d	-	71	0
107	..	..	1.3	1	+	98	91
104	..	..	1.3	1	+	97	94
72	FeBr ₂ 0.03	..	1.0	2	-	97	0
103	FeBr ₂ 0.01	..	1.3	1	+	100	0
112	Fe 0.32	15					
	FeBr ₂ 0.017		1.3	2	-	96	97
114	NiBr ₂ 0.0011	..	1.3	1	+	37	0
115	CoBr ₂ 0.0011	..	1.3	1	+	89	0
120	Fe 0.32	29	1.3	2	-	93	94
	NiBr ₂ 0.0011						
121	Fe 0.32	14	1.3	2	-	91	97
	CoBr ₂ 0.0011						
88	Sn 0.29	9	1.5	2	-	76	0
106	Sn 0.13	18	1.3	2	-	72	0
100	Sn 0.051	24	1.3	2	+	95	97
108	Sn 0.13	14	1.3	2	+	88	84
110	Fe 0.32	..					
	Sn 0.051	..	1.3	1	-	66	0
111	SnBr ₂ 0.013	..	1.3	2	+	68	0
119	Sn 0.051	75	1.3	2	+	99	97
	SnBr ₂ 0.009						
97	Cu ₂ Br ₂ 0.0042	..	1.3	1	+	43	0
105	Fe 0.32	19					
	Cu ₂ Br ₂ 0.0021		1.3	2	-	86	0
34	ZnBr ₂ 0.055	..	1.5	1 ^d	-	100	0
35	ZnBr ₂ 0.055	..	1.5	1 ^d	-	100	0
24	Zn 0.32	35	1.5	2 ^d	-	98	0
80	W 0.0055	1	1.3	2	-	36	0
91	Si 0.091	2	1.3	5	-	65	0
95	Tl 0.068	62	1.4	1	-	100	0

^aPer mol allyl bromide.

^bReaction at room temperature in the dark in the absence of light and solvents. All runs mechanically agitated except (d).

^cRemainder of addition product was 1,2-dibromopropane.

^dNo agitation.

TABLE 5--Continued

Expt. No.	Conditions of Addition					Products	
	Mols Added ^a Substance	Metal Reacted (Per Cent)	Mols HBr ^a	Time (Days) ^b	Air	Yield (Per Cent)	1,3-di- bromo- propane ^c (Per Cent)
43	Cu 0.30	54	1.5	4 ^d	-	65	0
44	Cu 0.30	30	1.0	4 ^d	-	59	0
76	Cu 0.020	59	1.3	1	-	68	0
96	Cu 0.019	55	1.3	1	+	47	0
109	(Cu 0.0097	..	1.3	1	-	64	0
	(Fe 0.32	..	1.3	2	+	60	0
98	Cu 0.019	68	1.3	2	+	60	0
85	As 0.078	39	1.3	2	-	27	0
94	Cd 0.33	26	1.3	1	-	37	0
99	Cd 0.086	100	1.3	4	+	39	0
87	Pb 0.35	25	1.5	2	-	39	3
102	Pb 0.060	100	1.3	4	+	45	0
74	Fe 0.32	6	1.3	0.1	-	100	96
73	Fe 0.02	18	1.3	0.7	-	90	94
31	Fe 0.32	23	1.5	4 ^d	-	97	26
79	Ti 0.13	13	1.3	1 ^e	-	99	30
83	Ti 0.13	16	1.3	1	-	95	26

^aPer mol allyl bromide.

^bReaction took place at room temperature in the absence of light and solvents, and was agitated mechanically unless indicated.

^cThe remainder of addition product was 1,2-dibromopropane.

^dNot agitated.

^eThe titanium powder used in these experiments was found to contain 1.7 per cent of iron.

thallium, tin, and tungsten were employed. It was found that these metals could be divided into several groups, depending on their rate of reaction with hydrogen bromide and the action of their bromides on the normal and abnormal additions.

Group 1 includes unreactive elements such as tungsten and silicon, which are scarcely attacked by the hydrogen bromide in reaction mixtures with allyl bromide. Neither of these elements or the small quantities of their salts formed had any appreciable effect on the rate or direction of addition (Expts. 80, 91).

Group 2 contains the metals zinc (24, 34, 35), thallium (95), and tin (88, 100, 106, 108, 111). These metals reacted rapidly with hydrogen bromide to form bromides which markedly accelerated the normal addition. Stannous bromide was found to inhibit abnormal addition initiated by air. The other halides were not tested directly.

In Group 3 are placed metals which reacted fairly rapidly with hydrogen bromide, but whose bromides did not appreciably accelerate the normal addition: copper (96, 97, 98), arsenic (85), cadmium (99), and lead (102). Since these metals and (by inference or test) their metal bromides were shown to inhibit air-initiated abnormal addition, it follows that the metals alone in vacuo should cause no abnormal addition.

Metals which cause abnormal addition, e.g., iron, nickel, and cobalt, are assigned to Group 4. These metals which were used in finely divided form slowly but continuously reacted with hydrogen bromide. It was demonstrated in Experiments 112, 120, 121 that ferrous bromide, cobalt bromide, and nickel bromide did not inhibit iron-initiated abnormal addition, although separate experiments (72, 115) showed that cobalt and ferrous bromides accelerated the normal addition somewhat.

To summarize, the conditions which must be fulfilled in order that a particular metal may initiate abnormal addition are: (1) the metal must react fairly slowly but continuously with hydrogen bromide, and (2) the metal bromide formed from the metal may accelerate normal addition to some extent, but it must not have an inhibitory effect on abnormal addition initiated by the metal (cobalt and nickelous bromides inhibit air-initiated, but not iron-initiated abnormal addition).

Then metals whose bromides are efficient inhibitors cannot cause abnormal addition. The fact that some metals, such as iron and nickel, do cause abnormal addition must be attributed to the fact that their metal bromides are inefficient in breaking the chains in the addition. This may arise from the insolubility or low activity of these bromides. Also whether some bromides (cobaltous and nickelous) are inhibitors seems to depend on the rapidity with which bromine atom chains are propagated. Thus these bromides are effective in breaking chains initiated by air, but are not effective when these chains are started from iron (115, 121; 114, 120; 103, 112). This indicates that more chains

arise from action of iron and hydrogen bromide than from the action of air and hydrogen bromide in the same time. Tin alone did not cause abnormal addition in the presence of stannous bromide, but, when the tin was reinforced by air, the combined action of the two chain generators was too rapid, and the stannous bromide no longer prevented the abnormal reaction (88, 119).

The inhibiting effect of metal bromides, and of the metals themselves, probably proceeds by a mechanism consisting of the absorption of bromine atoms.

It seems likely that conditions might be found under which any metal could initiate abnormal addition. Such conditions should exist if enough bromine atom chains were started so that complete addition occurred before appreciable amounts of metal bromide were formed to break the chains.

THE EFFECT OF IRON ON THE ADDITION OF HYDROGEN BROMIDE TO OTHER UNSATURATED SUBSTANCES

a) ALLYL CHLORIDE

Table 6 shows that iron initiated abnormal addition of hydrogen bromide to allyl chloride. The extent of this type of addition and the proportion of iron reacted paralleled closely similar experiments with allyl bromide.

b) VINYL CHLORIDE

The normal addition of hydrogen bromide to vinyl chloride in vacuo is usually obscured by the presence of small traces of peroxides, which are quite effective in promoting the abnormal reaction.¹⁹ Hence when iron was added to these reaction mixtures (55, 56) it was not possible to attribute the abnormal addition which occurred to the iron alone. Since diphenylamine would inhibit the action of traces of peroxides but would not, in the allyl bromide case at least, inhibit the action of iron, it was expected that additions of hydrogen bromide to vinyl chloride in the presence of iron and diphenylamine would show abnormal addition clearly attributable to the iron. However, only a small amount of the expected type of addition occurred, since diphenyl-

¹⁹ Kharasch and Hannum, J. Am. Chem. Soc., 56, 712 (1934).

TABLE 6

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL CHLORIDE,
VINYL CHLORIDE, PROPYLENE, ISOBUTYLENE, AND
STYRENE IN THE PRESENCE OF IRON

Expt. No.	Conditions of Addition					Products	
	Substance	Mols HBr ^a	Mols Fe	Fe Reacted (Per Cent)	Time (Days) ^b	Yield (Per Cent)	Abnormal Addition (Per Cent)
66	Allyl Cl ^c	1.5	0.29	29	4	91	38 ^c
67	Allyl Cl	1.5	0.29	33	4	95	36
55	Vinyl Cl	1.5	0.38	41	3	53	32
56	Vinyl Cl	1.5	0.26	22	3	68	46
61	Vinyl Cl ^d	1.5	0.26	33	3	99	4
62	Vinyl Cl ^e	1.5	0.26	23	3	20	0
122	Vinyl Cl ^f	1.5		..	3	84	5
123	Vinyl Cl ^f	1.5	0.26	9	3	92	87
57	Propylene	1.5	0.29	2	1	90	0
58	Propylene	1.5	0.29	12	1	87	0
59	Isobutylene	1.5	0.27	36	2	83	0
60	Isobutylene	1.5	0.27	36	2	100	0
117	Styrene ^g	1.5	0.27	5	0.2	100	0
118	Styrene ^g	1.5		..	0.2	100	0

^aPer mol allyl bromide.

^bReaction took place at room temperature in the absence of light, air, and solvents unless otherwise indicated.

^cComposition determined from refractive index.

1,2-chlorobromopropane 1.4811

1,3-chlorobromopropane 1.4861

as given in Robert S. Shane, "The Peroxide Effect upon the Addition of Hydrogen Bromide to Unsaturated Compounds," Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1933, p. 12.

^d3 mol per cent diphenylamine added.

^e3 mol per cent catechol added. ^fMechanically agitated.

^gIn pentane solution; 10 mols pentane per mol styrene.

amine and catechol both efficiently inhibited the abnormal reaction. The effect of iron was shown, however. Agitation caused the iron to be more efficient as a chain generator (123) than in the unagitated experiments (55, 56). Ferrous bromide demonstrated its inhibitory action on abnormal addition promoted by traces of peroxides (122). Now from the analogous situation with allyl

bromide the ferrous bromide should not be an inhibitor for iron-initiated abnormal addition, and hence the abnormal product resulting in the experiments in which iron alone was used must be attributed to the iron, since the action of peroxides would be inhibited by the ferrous bromide formed in the reaction mixture.

c) PROPYLENE AND ISOBUTYLENE

No abnormal addition was obtained by including iron in reaction mixtures with hydrogen bromide and propylene or isobutylene. Kharasch and Hinckley²⁰ showed that large quantities of peroxides were required to reverse addition to isobutylene, and Kharasch, McNab, and Mayo²¹ demonstrated that the same situation was true with propylene. The large quantities of peroxides were necessary to overcome the rapid normal addition of hydrogen bromide to these two hydrocarbons.

The iron had no reversing effect here, apparently because its action was insufficiently rapid or because of the accelerating effect of iron halides.

d) STYRENE IN DILUTE SOLUTION

Although the normal addition of hydrogen bromide to styrene is very rapid (complete in ten minutes even with oxygen present) Kharasch, Walling, and Mayo²² showed that abnormal addition occurred when the reaction was carried out in dilute solutions in the presence of added peroxides. When iron was substituted for the added peroxides, it was found in the present work that only normal addition took place.

The fact that iron initiated abnormal addition with allyl bromide and chloride (class 1) but not with hydrocarbons such as propylene, isobutylene, and styrene (class 2) may be explained in terms of relative rates of addition. When the normal addition is slow, any source of bromine atom chains is sufficient to produce reversal (e.g., normal addition in class 1 requires 10-13 days). However, if the normal addition is fast, reversal occurs only when

²⁰ Kharasch and Hinckley, J. Am. Chem. Soc., 56, 1243 (1934).

²¹ Kharasch, McNab, and Mayo, ibid., 55, 2531 (1933).

²² Kharasch, Walling, and Mayo, ibid., 61, 2693 (1939).

normal addition is outrun by an even faster abnormal addition. The normal addition of hydrogen bromide to the hydrocarbons seems to be too fast (1-3 hours) to permit the iron to initiate abnormal addition. Another possible explanation is that effective free radicals are generated by reaction (c) on page 8, and that hydrocarbons cannot give this reaction.

EXPERIMENTAL PART

PURIFICATION OF 1,2- AND 1,3-DIBROMOPROPANE

Propylene dibromide (1,2-dibromopropane) was prepared in two ways. (1) Pure bromine and propylene gas were added simultaneously and slowly to a little liquid propylene at -80° . This product was washed with water several times and dried over potassium carbonate. (2) Fractionation of a mixture of several hundred grams of allyl bromide-hydrogen bromide addition products permitted recovery of both 1,2- and 1,3-dibromopropanes. Both of these samples were free of chlorides, because C.P. bromine was used throughout. Propylene bromide from each source was carefully fractionated through a Podbielniak column, and 8-10 fractions cut out. Every fraction from each source showed the same refractive index, with an Abbé-type refractometer: (n_D^{20}) 1.5200. The low refractive index reported by Kharasch and Mayo²³ is thought to be due to the presence of bromohydrins or chlorides in their product.

Trimethylene bromide (1,3-dibromopropane) from a commercial source showed a small boiling point range but considerable variation in refractive index when fractionated. The water solubility of some fractions indicated the presence of trimethylene bromohydrin. However, removal of this impurity by washing with cold concentrated sulphuric acid and fractionation of the washed product through a Podbielniak column produced ten fractions of approximately the same boiling point (71° at 30 mm.) having the same refractive index: 1.5230. Similarly, fractionation of recovered addition products finally yielded ten fractions of constant boiling point. The refractive index of the first seven was 1.5230, and of the last three 1.5231. The higher value has been

²³Kharasch and Mayo, loc. cit.

taken as the more probable one, and has been used in all calculations in this paper. A Bausch and Lomb test prism having a value 1.5000 was used to check the refractometer employed in these measurements.

PREPARATION OF UNSATURATED COMPOUNDS

Allyl bromide and allyl chloride were prepared by the method of Dewael.²⁴ If peroxides were present, they were removed by shaking with ferrous sulphate acidified with sulphuric acid and distilling from phosphorus pentoxide. A sample of allyl bromide treated in this manner was carefully fractionated, and the first, middle, and last fractions all had the same refractive index: 1.4695. Isobutylene was prepared from tertiary butyl alcohol and oxalic acid. Vinyl chloride, propylene, and styrene (antioxidant removed by vacuum distillation) were obtained from commercial sources.

Reduced iron was obtained in the powdered form from Merck and Company, and reduced with dry, oxygen-free hydrogen immediately before use. It was essential that no other metals be present in the iron in sufficient quantities to act as inhibitors, although no trouble was experienced with the above sample. The finely powdered iron was placed in a clean Pyrex tube of 10 mm. inside diameter, open on both ends, and heated to a temperature just below a dull redness in a current of hydrogen for an hour. After the tube had cooled in a current of hydrogen, the iron was removed, weighed out into a bomb tube, evacuated to 10^{-5} mm., and heated for fifteen minutes. Purified hydrogen was let into the system, and pumped out after fifteen minutes, keeping the iron at a temperature of 350°C . This evacuation and replacement with hydrogen was done several times, and finally the evacuated bomb tubes were allowed to cool, and stored under vacuum until used.

In general, 0.1 mols of unsaturated compound were used for 0.03 mols of iron or other metal, although this proportion was varied in some experiments.

TECHNIQUE

The usual vacuum technique developed in this laboratory

²⁴Dewael, Bull. soc. chim. belg., 59, 40 (1930).

by Kharasch and Mayo,²⁵ in which sealed bomb tubes evacuated to 10^{-5} mm. were used as reaction tubes, was employed throughout the present work. Hydrogen evolved from metals in the reaction mixtures was measured approximately in some cases by cooling the unopened bomb tube in liquid nitrogen, connecting the small tip to a calibrated, evacuated system, breaking the tip, and measuring the increase in pressure within the system. The organic products were removed from the bomb tube by distillation, and the inorganic residues extracted with water or alkali, depending on the metal bromide present. The extractions were diluted in a 250 ml. volumetric flask and aliquots taken for analysis for bromide by the Volhard method. Rough agreement was found between the amounts of hydrogen and of bromide ion formed in reactions involving metals.

Analysis of mixtures of dibromopropanes was carried out by fractionation through a Podbielniak column at 30 mm. pressure. This effected a complete separation of allyl bromide from the dibromopropanes, and produced temperature-volume curves which permitted a rough check to be made on the compositions of dibromopropane mixtures given by refractive index measurements. This method has the advantage over the dimethylaniline procedure previously used²⁶ when the fractionating column was not available, because it allows quicker and more effective separation of allyl bromide from mixtures in which fairly large amounts of this component were present. A comparison of the two methods was made in several instances by dividing reaction products into two parts, and analyzing it by both methods. Table 7 shows that the results obtained by the two methods are substantially in agreement.

CONCLUSIONS

Although the results obtained in the present work confirm the experimental reports of Urushibara and Takebayashi, new facts have been uncovered which throw an entirely different light on the mechanism by which metals initiate abnormal addition. The occurrence of hydrogen and metal bromides in the reaction products of additions in the presence of metals has demonstrated that this mechanism is not a catalytic one, while the demonstration that metal bromides are inhibitors has focused attention on hydrogen

²⁵Kharasch and Mayo, loc. cit.

²⁶Ibid.

TABLE 7

COMPARISON OF ANALYTICAL METHODS

Expt.	Allyl Bromide (Per Cent)	Index of Refraction after Removal of Allyl Bromide by:	
		Dimethylaniline Method	Distillation
1	6	1.5219	1.5219
8	8	1.5200	1.5200
36	25	1.5189 ^a	1.5200
37	39	1.5188 ^a	1.5200
38	29	1.5191 ^a	1.5200

^aThe product with this index was redistilled and the first 0.2 cc. collected separately (index 1.5040). The rest of the distillate had index 1.5200. This indicated incomplete removal by the dimethylaniline method when 25-40 per cent allyl bromide was present.

as the important initiator in the abnormal reaction chain when metals are present. The efficiency of a metal bromide as an inhibitor has been shown to be very important, since certain metals were found not to cause abnormal addition, possibly because their metal bromides acted as chain breakers. Experiments with several unsaturated compounds indicated that the effectiveness of iron in inducing reversal of addition varies, depending to a great extent on the rapidity of the normal addition which it must reverse.

It was concluded that (1) the iron-induced addition of hydrogen bromide to allyl bromide is a chain reaction involving bromine atoms, each chain being initiated by a hydrogen atom or an organic radical, and that (2) several other metals fail to give a similar effect because (a) their halides are either strong enough catalysts for the normal addition or (b) strong inhibitors of the abnormal addition, or (c) because the metals do not react with hydrogen bromide at a suitable rate.

SUMMARY

1. A study of the effects of metals on the addition of hydrogen bromide to unsaturated substances has revealed that

metals may cause abnormal addition which can be inhibited by metal bromides and organic antioxidants, and that metals will not initiate abnormal addition when the speed of the normal addition is very fast.

2. The defects of a physical explanation for these phenomena have been clearly demonstrated.

3. The results were explained in terms of a chain reaction mechanism for abnormal addition, initiated by hydrogen atoms or organic radicals, and carried along by bromine atoms. Inhibition was explained as a rupture of links in the reaction chain by collision of the chain carriers with molecules of metal, metal bromide, or organic antioxidant.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the friendly advice and many helpful suggestions given him by Drs. M. S. Kharasch and F. R. Mayo, whose encouragement during periods of difficulty did much to make this work possible.

